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STUDY OF THE GROWTH PARAMETERS INVOLVED IN SYNTHESIZING BORON CARBIDE FILAMENTS

1st Quarterly Report

by

A. Gatti

C. Mancuso

E. Feingold

J. Kitler

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Space Sciences Laboratory
Missile and Space Division
General Electric Company
P.O. Box 8555, Philadelphia 1, Pa.

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I. SUMMARY

The present program, which is a continuation of a study sponsored by NASA on contract NASw 937, is concerned with:

(1) Growth of Boron Carbide Whiskers

(2) Characterization of these whiskers in terms of physical and chemical properties

(3) Incorporation of these whiskers in composites

Studies were continued on investiating the effects of the growth and deposition zone geometry on whisker production. The results based on several different mandrels and chimney arrangements indicate that the chemical and physical gradients in the furnace are grossly influenced by these geometric parameters.

An extended run under "standard" conditions has produced whiskers of an unusual appearance. Characterization of these whiskers in terms of growth direction and degree of crystalline perfection is presently being completed. Preliminary inspection of these whiskers indicates that heavy "overgrowths" are present.

A major effort was made to fabricate B_4C-aluminum composites by hot pressing techniques during the present report period. Strength values in the order of 20,000 psi are the greatest obtained to date. While this method seems superior to previous infiltration techniques, from a fabrication viewpoint, further refinements will be necessary in order to improve the quality and strength of the composites.

An apparatus has been built and is presently being calibrated to conduct elevated temperature tensile tests of B_4C whiskers. The preparation for these tests is in the final stages.

II. INTRODUCTION

B_4C whiskers exhibit attractive properties for utilization in composite materials. In terms of high strength, low density and high elastic modulus, these whiskers when utilized as reinforcements offer great potential for high strength-to-weight or high stiffness-to-weight materials for future applications. Their refractory properties, in addition, make them also valuable for high temperature applications.

The present program is a continuation of experimentation in:

1) The scale-up of whisker production.
2) The testing of individual whiskers at high temperature.
3) The fabrication and testing of composites containing B_4C whiskers.

A. OBJECTIVES AND APPROACHES

1. Growth

Although more than one method of B_4C whisker growth has been studied, the most successful to date has been the pure vapor method[1, 2]. This method consists of the vaporization at high temperature of B_4C powder and the subsequent condensation of B_4C whiskers on a graphite substrate at a lower temperature. This method has been used almost exclusively to study the growth parameters and to obtain an adequate whisker supply in order to pursue the objectives of this program.

2. Strength

Fabrication of equipment for testing individual whiskers at high temperature has been completed. Calibration of the equipment is presently being accomplished and the testing of whiskers at high temperature in bending is expected to proceed in the near future.

3. Structure

Extensive work on the investigation of crystalline perfection of the as-grown B_4C whiskers has been reported previously[1]. Subsequently, some interesting and unusual whiskers have been grown and are presently under investigation. Since the high degree of perfection of the whisker-like crystals is believed responsible for their high strength, this study is possibly the most important phase of this program.

4. Composite Studies

Since the utilization of these B_4C whiskers as a reinforcement in composite materials is the ultimate long range goal of this investigation, it is necessary to study promising methods of fabrication in order to establish the critical problems involved in the fabrication of B_4C whisker composites. A former study[1] of metals which form chemically compatible matrices and at the same time possess attractive mechanical properties for use in composites, led to the decision to work with aluminum and Fernico "5" (50% iron, 25% nickel, 25% cobalt alloy.).

During this report period, only aluminum-B_4C composites were fabricated. Since aluminum has the advantage of a low melting point, experiments can proceed without the problems encountered at higher temperatures, such as increased rate of reaction with die materials, etc.

The efforts expended during the present report period have been fruitful, and have extended the state of knowledge concerning B_4C whisker technology. Significant achievements have been made both in growth studies and in composite fabrication and testing studies.

III. EXPERIMENTAL PROCEDURES AND RESULTS

A. GROWTH STUDIES

1. Description of Equipment

Growth studies were performed in a graphite resistance furnace which has been adequately described in former reports[1]. Systematic changes have been made in the geometry of the deposition zone and these will be discussed.

2. Growth of B_4C Whiskers

Since major emphasis was placed on composite fabrication and testing, large quantities of good quality whiskers were grown utilizing the now-standard* pure vapor technique. Variations in geometry of deposition mandrels and chimneys were also studied in order to further optimize growth in terms of quality and quantity.

Experiments were performed with a conical chimney, described previously[3]. Whisker quality and quantity were comparable to the standard runs utilizing a cylindrically shaped chimney and internal mandrel with a baffle. Figure 1 shows a typical result. The conical shape of the mandrel has modified the gradient so that the deposition zone for B_4C whiskers is a much sharper and narrow band. Further work with this chimney and other variations is contemplated.

Control experiments which were conducted to further ascertain the effectiveness of vanadium addition to catalyst depleted batches of B_4C powder gave continued indication that the addition of vanadium does, indeed, cause whiskers to grow from a previously exhausted B_4C powder charge.

An extended run under these now standard conditions led to an unusual whisker product. A photograph of the results of this run appears in Figure 2. These whiskers are currently being studied to determine orientation and degree of perfection and will be reported on in another section.

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*Standard conditions are: B_4C vaporization temperature 1900°C, whisker growing temperature 1700°C, pressure 125μ, time 5 hours.

Figure 1. Standard B_4C Whisker Vat Using Conical Chimney and Internal Mandrel.

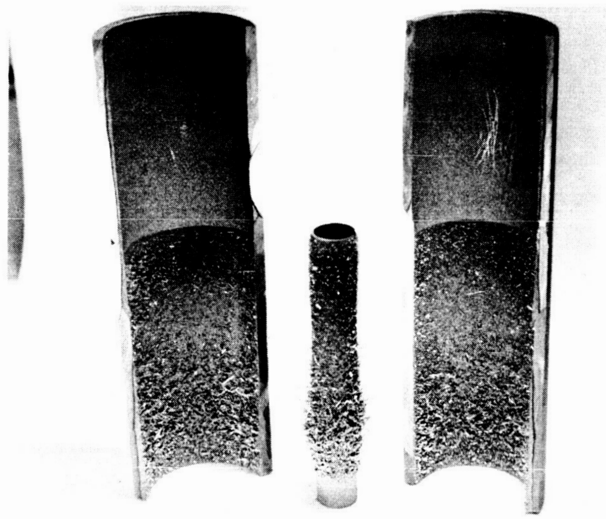


Figure 2. Results of Extended Standard Run.

B. MECHANICAL PROPERTIES OF B_4C WHISKERS

An apparatus has been designed, built, and partially tested for conducting 3-point bend tests on short lengths of whiskers at both room and elevated temperatures. The equipment is a modification of the type used by Pearson, et al[2], and has been described in previous NASA Quarterly Reports[3].

Calibration of the apparatus is in progress, in order to evaluate the sensitivity of the system. Bendtests were performed on .001" diameter tungsten wire to compare measured values of the modulus with the known value of 53×10^6 psi. Although some initial test runs fell within 10% of the accepted value, the average value obtained for 15 tests was 39×10^6 psi which corresponds to a 25% error. Extraneous stresses were suspected of being the primary cause of this error. For example, the connection between the quartz filament and the cantilever was rigid, making it possible to transfer biaxial and triaxial stresses to the fiber during testing. An attempt to eliminate these extraneous stresses by incorporating a flexible section in a tensile member of the system resulted in considerable improvement. Modulus values for tungsten were then measured to ± 5%.

Since an effective technique for bend testing of fine, (about 1 mil diameter) uniform wire has been developed, it was decided to utilize alumina whiskers for initial experiments, since they offer several advantages over B_4C whiskers at the present time: (1) They are currently available in a wide variety of sizes including the range desired, (2) Their properties as to size, shape, strength, and modulus have been more carefully characterized, (3) The polishing of a cross-section of a mounted alumina whisker is much simpler than that of a B_4C whisker, since the B_4C whiskers are harder and more difficult to polish.

Alumina whiskers of approximately $600\mu^2$ cross sectional area and free of gross surface defects were carefully selected. The whiskers were bent in the flexure apparatus and the unfractured samples were mounted and polished in a clear epoxy matrix in order to observe and measure their cross-sections. The moment of inertia was calculated by assuming the whisker to be laying in its stable equilibrium position during bending. The modulus was calculated from the standard relation

$$E = \frac{P}{\delta} \frac{\ell^3}{48 I}$$

where:

E = modulus of elasticity in psi

P = load in pounds

δ = deflection in inches

ℓ = span length between bending supports in inches

I = moment of inertia in inches to the fourth power

For the two whisker samples tested to date, measured moduli have been in error by 25%. Factors known to influence the modulus measurement such as whisker taper, poor alignment, etc. are currently being evaluated. Further work on the apparatus must be done before sufficient refinement necessary to give meaningful data is attained.

C. B_4C WHISKER CHARACTERIZATION

An extended run (20 hours) beyond the standard time (5 hrs) resulted in unusual whisker growth, as shown in Figure 2. The whiskers ranged from very coarse and curved varieties located in positions near the high temperature end of the reaction chamber to smooth fairly straight varieties located in positions near the cooler end. The whisker deposit is shown schematically in Figure 3. It is convenient to arbitrarily delineate 3 regions or zones in this Figure. Zone I, contained extremely coarse curved whiskers with heavy surface deposits; Zone III, contained fairly smooth almost straight whiskers; and Zone II, contained an intermediate variety of whiskers.

The coarse curved whiskers were weak and survived only the most gentle handling, the smooth straight whiskers appeared to be much stronger.

1. Model for Whisker Growth Using Concentric Cylinder Reactor Geometry

Previously[3], a mechanism for B_4C whisker growth was presented. An extension of this mechanism will now be used to explain the observed character of the whiskers produced in the extended run.

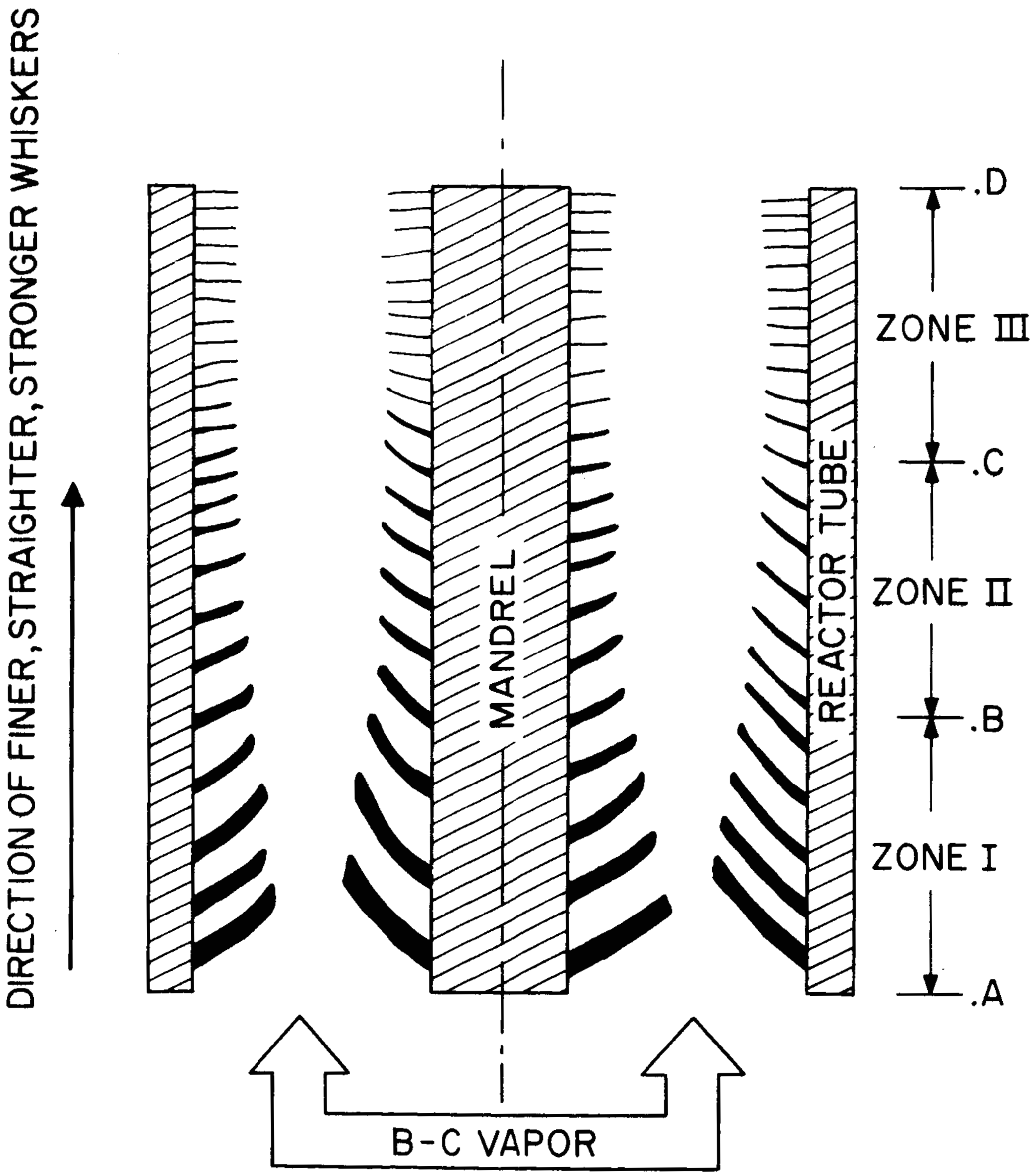


Figure 3. Schematic Representation (Not to Scale) of Concentric Cylinder Whisker Growth Chamber Showing Types and Locations After an Extended (20 hour) "Normal" Run.

In Figure 4 is shown a schematic representation of the temperature distribution* within the annular region of the concentric cylinder reaction chamber. Shown in section in Figure 4 are (a) the face of the internal mandrel and (b) the inside face of the reactor tube. The smooth saddle like lines represent isotherms, the lower temperature isotherms (i.e., T_1) are at the top of the Figure. As one proceeds to the lower portions of this Figure the isotherms represent higher temperatures (i.e., $T_1 < Tc < T_2$). Although shown as lines in this diagram one must realize that due to the cylindrical symmetry of the reactor that each isotherm represents a surface of revolution. The surfaces so produced are those of distorted semi-toroids. Since each isothermal surface corresponds to a different state of vapor super saturation, the isotherm surfaces can be considered to represent isoconcentration surfaces. That is, for $T < Tc$ the supersaturation level is too high for regular whisker growth, see reference [3]. The dashed lines in Figure 4 are temperature gradient lines (e.g. normal to the isotherms). The diffusional energy gradients of vapor species are parallel to the temperature gradients. That is, the diffusional energy distribution, necessary for whisker growth, causes vapor species migration parallel to the temperature gradient.

Therefore, whisker growth is expected to proceed in the direction of maximum change of supersaturation, that is in the direction of the gradients. Indeed this is observed, see Figures 2 and 3. Whisker growth continues until the whiskers reach the critical isoconcentration surface (corresponding to the Tc isotherm), whereupon regular growth ceases.

The net motion (direction) of the vapor species is of course from the bottom (hot) end of the reactor to the top (cooler) end. The concentration of the reactants (the vapor) becomes depleted in the formation of whiskers at the hot end. Therefore, the whiskers in the cooler portion

* The temperature distribution as discussed here has been estimated but is believed to be qualitatively accurate. Future work will be done in order to map the actual thermal contour of the reaction chamber.

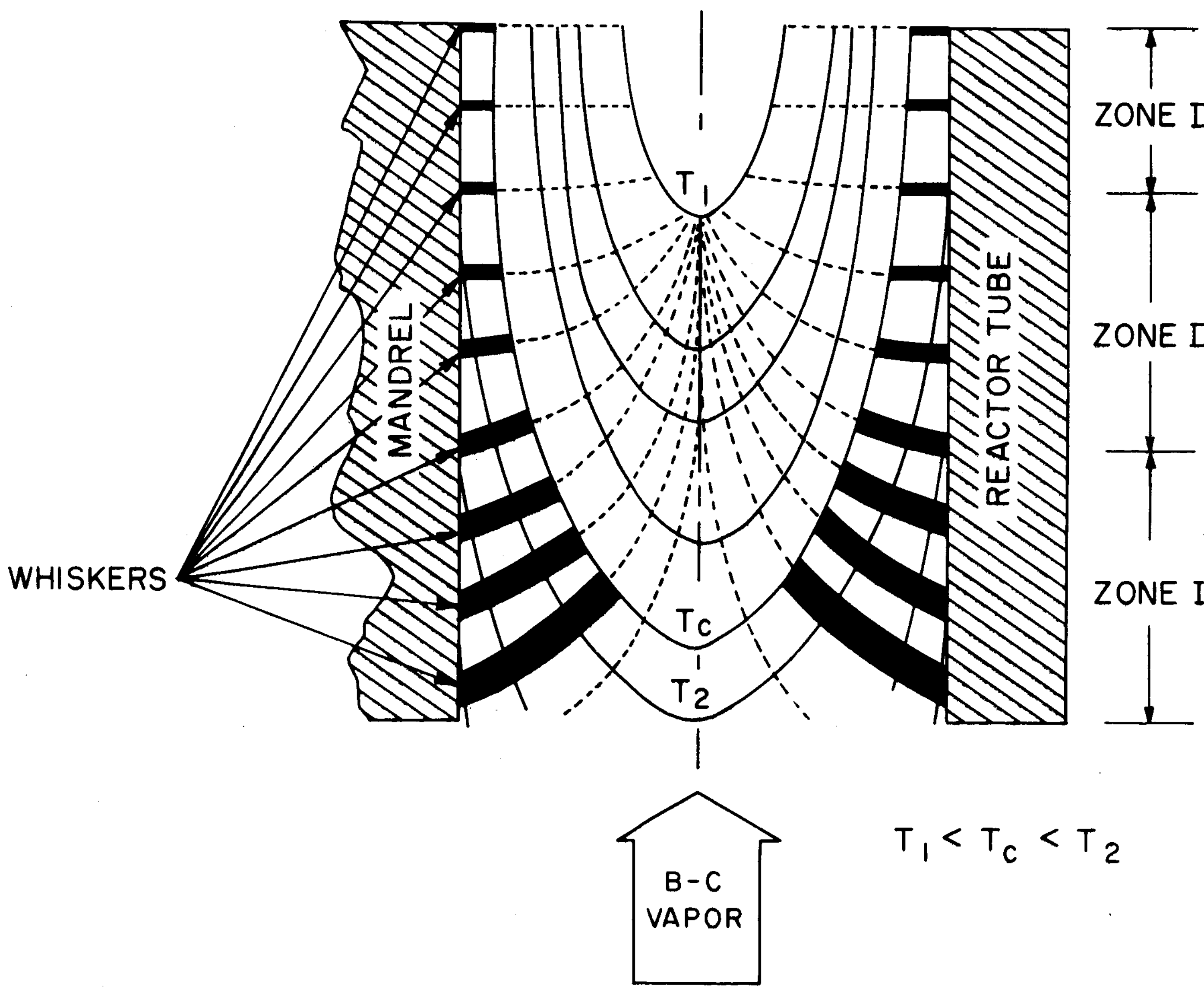


Figure 4. Schematic Representation of Temperature Distribution in the Annular Region of the Reaction Chamber. (Continuous lines are isotherms, dashed lines are parallel to temperature gradients).

of the reactor grow at a much slower rate since only those reactant species which have avoided the whisker growth process in the hot end are available for whisker growth in the cool end.

The above discussion explains, (a) the differences in curvature observed in the whiskers in Zones I, II and III, (b) why the whiskers in the 'hotter' sections are coarser than those in the 'cooler' regions, (c) the variation in whisker length in zones I, II and III. These facts are common to all whisker batches grown in the cylindrically symmetrical reactor.

In an extended run, such as the one being described here, the chances for the erroneous incorporation (non-periodic) of condensing vapor species is greatly increased, especially in the region(s) where the concentration of reaction species is the greatest, namely, in the 'hotter' portions of the reactor. The 'out-of-step' incorporation of material causes the whiskers so effected to exhibit heavy surface deposits. Also of high probability in an extended run is the incorporation of nucleation sites on mature whiskers. When this occurs, branches or dendrites appear on the whiskers so effected, see Figure 5. In the next section the nature of the surface deposits will be discussed.

2. Character of Surface Deposits

In Figure 5, 6, and 7 photomicrographs are presented of some typical surface deposits found on the whiskers from the higher temperature zones (corresponding to zones I and II in Figures 3 and 4) of the reactor chamber. This type of deposit is not normally observed on the whiskers from short (normal, 4 hour) runs. The reader is referred to Figures 11, 12, and 18 in reference 3 in which 'normal' whiskers are depicted. Close examination of the higher magnification photomicrographs (Figures 5-B, 6-B, 7-B) show that the surface deposits reflect the orientation of the substrate (epitaxy). That is, they are not randomly oriented. In Figures 5-A and -C, a dendrite can be seen to emerge from the surface of a mature, curved whisker (see Section 1).

X-ray diffraction photographs were made of several whiskers which contained surface deposits. Each diffraction pattern exhibited a common feature: a poly-crystalline B_4C deposit with a high degree of preferred orientation.

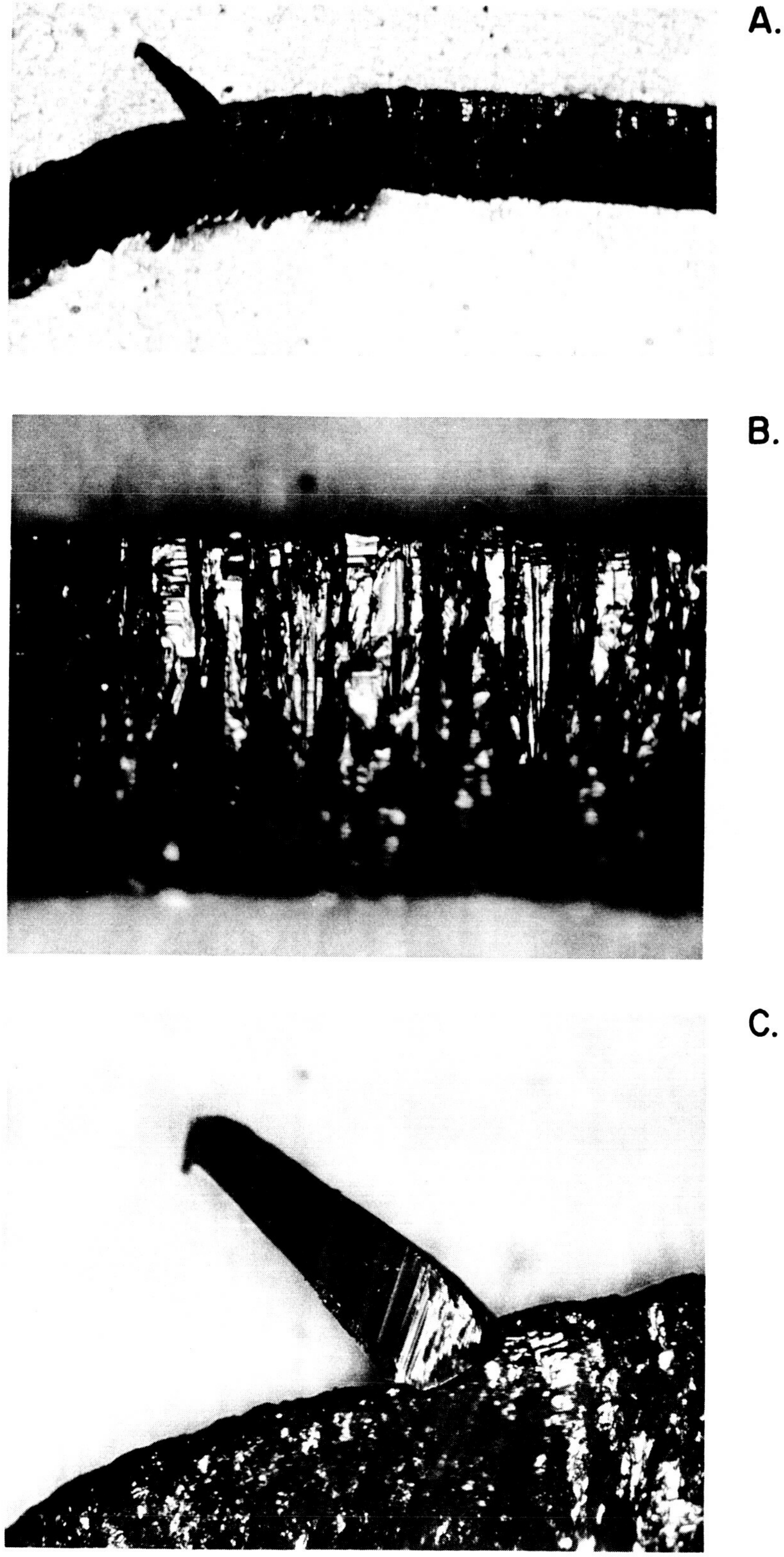
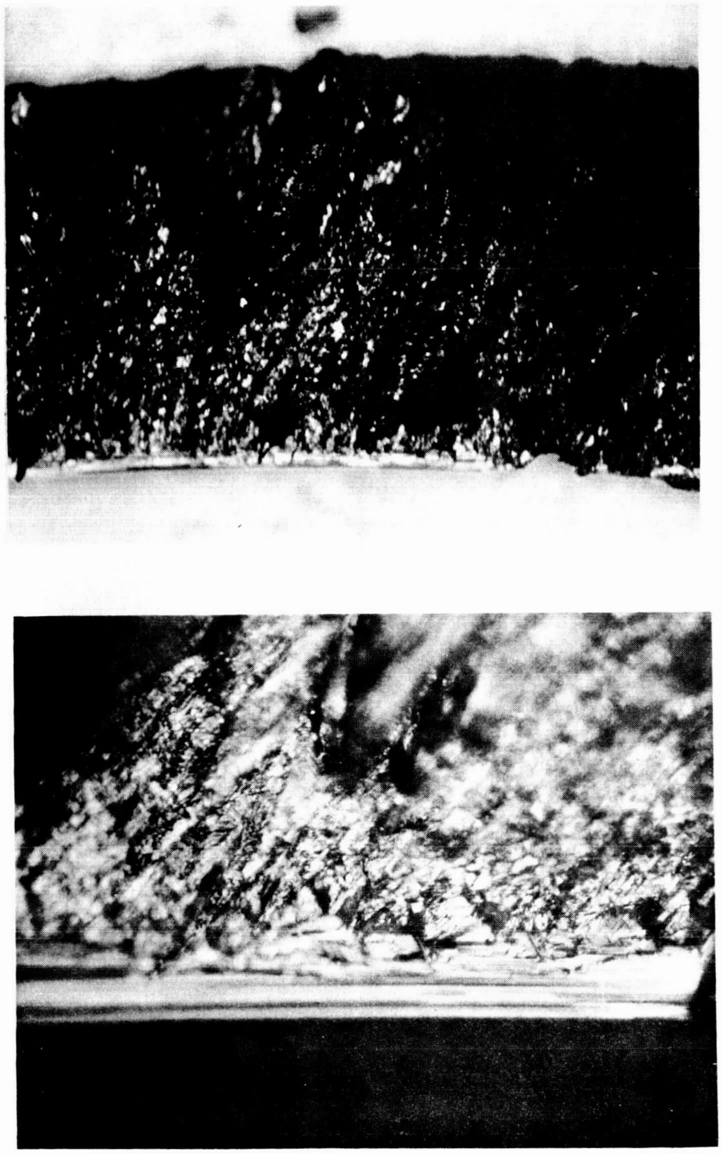


Figure 5. Whisker from Zone I of Reactor. Note Curvature of Whisker, Rough Surface Deposits and Dendrite. Magnification: A = 45X, B = 163X, C = 163X.



A.

B.

Figure 6. Curved Whisker from Reactor Zone I Showing Heavy Surface Deposits. Note That the Orientation of the Substrate is Carried Through in the Surface Deposits. (Magnification: A = 80X, B = 320X.) B is a Region of A.

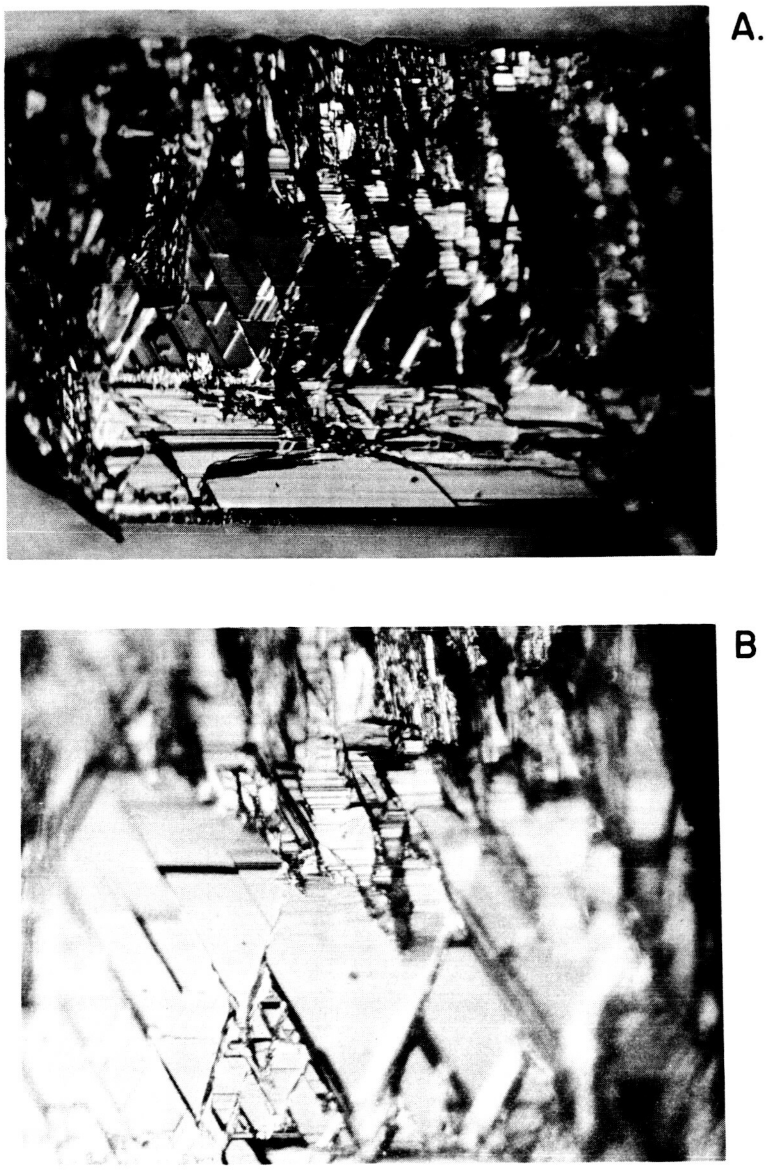


Figure 7. Whisker from Zone II of the Reactor. B is an Enlarged Portion of A. Note the Register (Orientation) of the Deposit with the Substrate. (Magnification: A = 160X, B = 320X).

Figure 8A is an x-ray diffraction photograph (layer-line pattern) obtained from a whisker from region III of the reaction chamber. The rather sharp spots indicate that the specimen is of a near-single-crystal character. The pattern is typical of a B_4C whisker with a $\langle 100 \rangle$ axis orientation[3]. Close examination of the low angle diffraction region reveals fine, low intensity, discontinuous diffraction rings. Since they pass through B_4C diffraction spots, the material which gave rise to these reflections was B_4C. That the rings are recognizable indicates that the material is polycrystalline. That the discontinuous intensities peak in the regions of the single crystal diffraction spots indicates that the deposited polycrystalline B_4C is very nearly oriented in the same direction as the single crystal substrate.

Figure 8B is an x-ray diffraction photograph obtained from a relatively straight portion of a whisker which contained heavy surface deposits from region I of the reactor. Here the high intensity diffraction rings of non-uniform intensity indicate: (a) that the sample is composed of a relatively massive polycrystalline deposit, and (b) that the deposit has a high degree of preferred orientation.

3. <u>Internal Strain in Curved Whiskers</u>

It is quite natural that a curved crystal be strained, for only through adjustments of interatomic separations can a crystal of finite size be curved. This is shown schematically for a two dimensional cubic crystal lattice in Figure 9. Note: B_4C has an hexagonal structure. Figure 9-A shows an unstrained straight crystal, whereas Figure 9-B shows that adjustments of interatomic separations must be made in the case where the crystal is curved. The uniform interatomic separation is a_o. In the curved crystal where the interatomic separation is a_t ($a_t > a_o$) the crystal is under tension, and where the separation is a_c ($a_c < a_o$) it is under compression. If the curvature is severe, then the system is unstable and a small disturbance can cause catastrophic failure. This has been observed. When whiskers of very high curvature are gently disturbed they will often shatter.

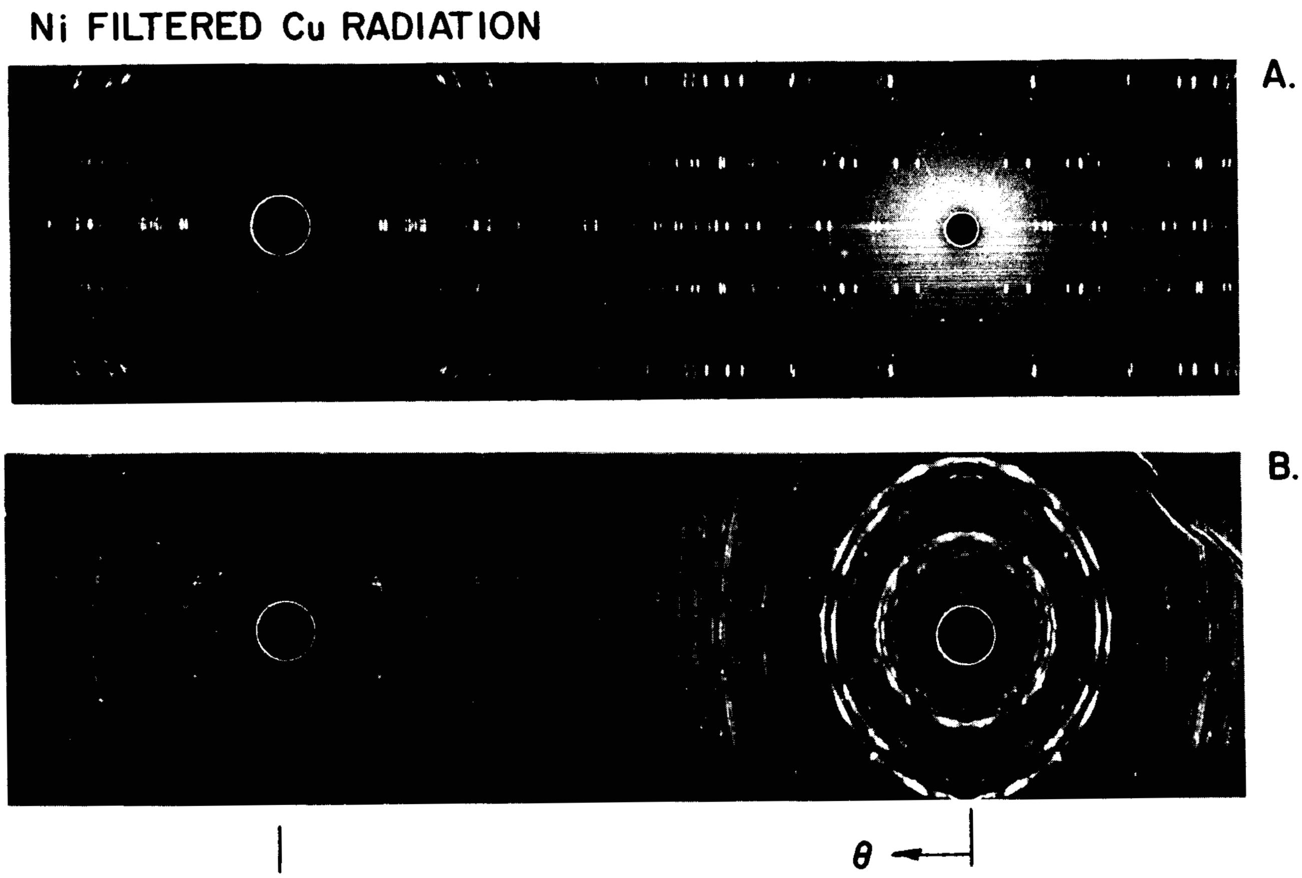


Figure 8. A. X-ray Diffraction Pattern from Whisker Taken from Zone III of the Reactor.
B. X-ray Diffraction Pattern from Whisker Taken from Zone II of the Reactor.

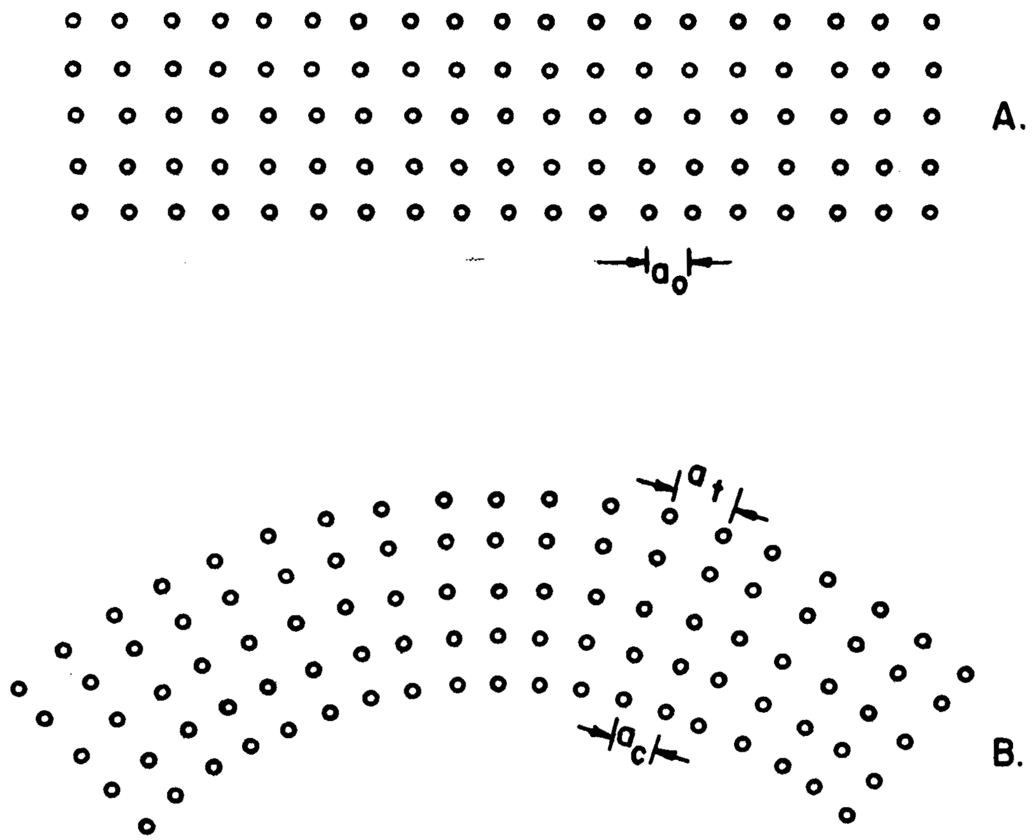


Figure 9. A. Unstrained Straight 2-Dimensional Crystal.
B. Same Crystal Bent, Showing Readjustment of Atomic Separations Required to Accommodate Bending.

At the present time, x-ray diffraction determinations of lattice strains in curved whiskers are being determined. This will be discussed in a later report.

D. COMPOSITE STUDIES

Composite fabrication studies during the present reporting period were performed utilizing conventional and modified hot-pressing techniques. Conventional hot-pressing was done in a steel heat-resistant die* capable of operating at temperatures as high as 600°C for extended periods. Its unique design minimizes and simplifies the number of parts necessary to function and also requires only punch changes and one half-a-die change in order to shift from one specimen cross-section to another. Thus, specimens can be fabricated with cross-sections varying from 1/8" x 1" to 1/16" x 1" with a minimum of shop time expended. Figure 10 is a photograph at about 1/2 size of a typical die which utilizes a 1/8" x 1" punch cross section. The modified hot pressing is being performed in "Speer" graphite dies of the same design as the steel die of Figure 10 .

1. Specimen Preparation and Fabrication

Specimens were prepared by the following techniques:

(a) A given quantity of B_4C whiskers was weighed out. A sufficient quantity of -100 mesh Al powder was added to the whiskers so that the volume percent whiskers was 20%. The resulting mixture was then put into a hot pressing die and hot pressed at 2000 psi in a graphite die at 600°C. The specimens using this simple direct approach were not of good quality. Good mixing of the two phases was not possible because of density, size and shape differences. Also, during subsequent fabrication, bridging of whiskers occurred which resulted in excessive whisker breakage leading to cracked and non-densified composites.

(b) Superior specimens were prepared by a modification of the above technique which can be best described as a sandwich technique. The same basic technique is used maintaining the same weight of whiskers and aluminum powder, but in addition, a layer of aluminum powder is placed on the top and bottom of the composite mixture which eliminated direct die

* Peerless "A"

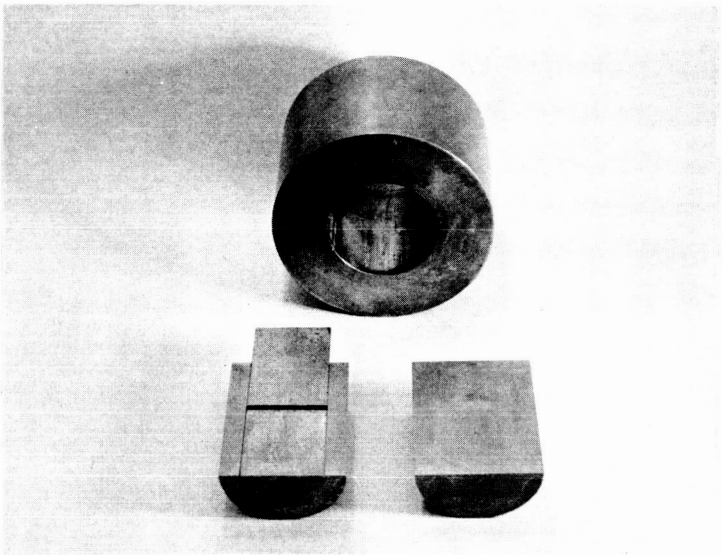


Figure 10. Steel Die Used to Hot Press Aluminum - B_4C Whisker Composites - About 1/2 Size.

pressure on the composite. The composite was easily tested by filing away the excess aluminum left by the sandwiched structure. Excess aluminum was left on the ends of the specimens since it made ideal gripping surface for tensile grips. A schematic diagram of the fabrication sequence is shown in Figure 11. The whisker breaking problem was thus minimized but still prevailed because individual whisker to whisker contact was not eliminated.

(c) A final and most successful technique for forming Al-B_4C whisker composites utilized flake aluminum in conjunction with -100 mesh atomized aluminum. A slurry of B_4C whiskers and flake* aluminum was made using acetone as a vehicle. The Al flake size is such that wetting of individual B_4C whiskers by the slurry was easily accomplished. The mixture was then dried and a sandwich formed and hot pressed. A typical microstructure of a B_4C-aluminum composite formed by this technique is shown in Figure 12.

Preliminary hot pressing studies were performed in graphite dies at temperature below 660°C (m.p. of Al), at pressures not exceeding 4,000 psi. These conditions did not prove feasible for producing dense specimens in reasonable times. The pressing schedule was then revised so that the die temperature reached 700°C. This was sufficient temperature to melt the aluminum metal of the composite sandwich extruding excess liquid metal out of the die. Such a modification of the conventional hot pressing technique could better be described as pressure infiltration since excess metal is added to a composite which is ultimately squeezed out leaving behind a dense, high volume fraction composite.

A further refinement of the die loading technique involves the substitution of a grooved lower punch in the graphite die, adding the whisker-Al mixture and vibrating. The steep walls of the grooved punch tends to align the whiskers so that they will be oriented more parallel to the tensile axis after fabrication. A conventional punch is added to the top of the die so that the die can be turned over and the grooved punch removed before sandwiching.

*Pigment grade, flake size .1μ thick x 20μ x 2000μ.

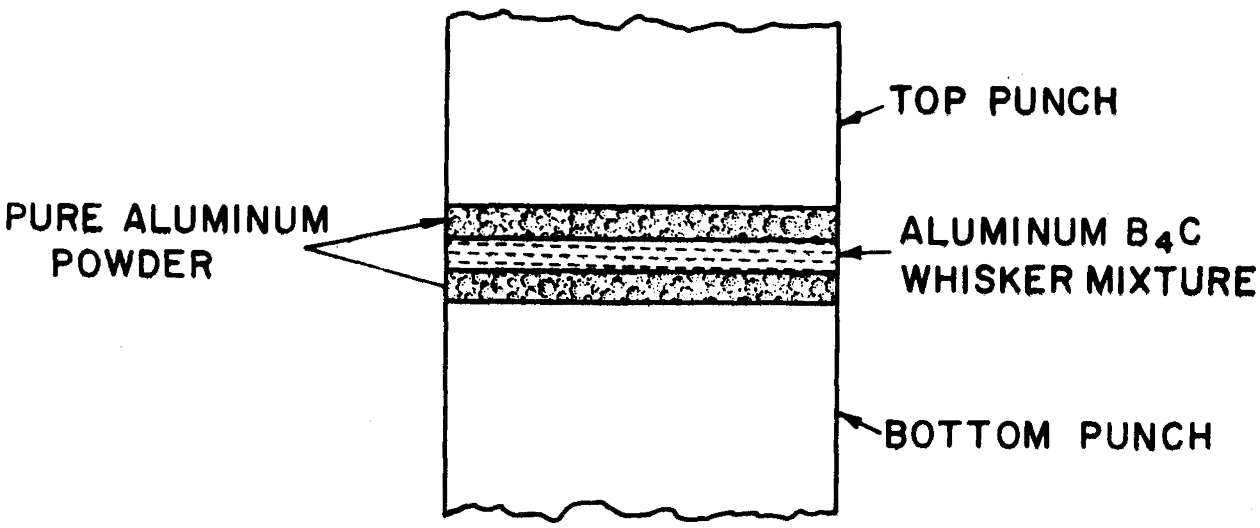


Figure 11. Schematic Diagram of Fabrication Sequence Followed to Produce "Sandwich" Specimen.

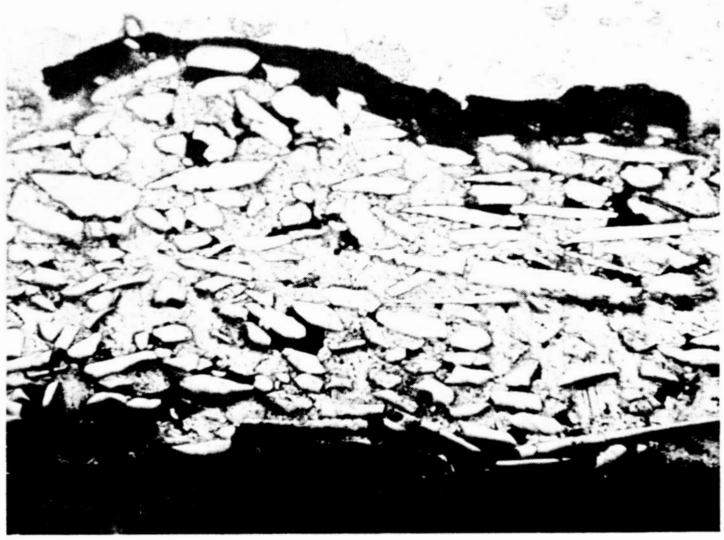


Figure 12. Typical Microstructure at 75X Forged by "Sandwich" Technique in Conjunction with Aluminum Flake - B_4C Whisker Slurry.

Since it was obvious that conventional hot pressing in graphite was not possible, steel dies of similar design were used together with the sandwich technique described in section C.

2. Results and Discussion

Tensile data derived from successful composites formed by both fabrication methods are summarized in Table I. Testing was performed on an Instron tensile machine utilizing air grips to hold the specimens in position. As can be seen from Table I, no composites with exceptional strength are as yet a reality. Many factors remain to be controlled before the potential reinforcing ability of B_4C whiskers will be reached. Among these factors are:

(1) Selection of the higher strength whiskers for incorporation into composites (the present results utilized all whiskers available)

(2) Ascertain and control (by coating, etc.) any reactions occurring on the whisker surfaces during fabrication.

(3) Improve testing techniques so that no bending is superimposed on the composites while tensile testing.

IV. CONCLUSIONS

Further studies on geometric parameters which can affect B_4C whisker growth have been made utilizing a cone-type configuration. Such a system tends to sharpen the deposition temperature gradient (and therefore zone) to nearly a sharp line, decreasing whisker nucleation.

Although no high strength composites have yet been fabricated, a technique has been developed which produces aluminum-B_4C composites of theoretical density containing a high volume fraction of B_4C whiskers. Experience gained during this quarter has contributed toward a better understanding of the problems associated with composite fabrication and will be most useful in planning and performing future work.

Further experimentation with the hot bend testing apparatus has shown that such tests can be successfully performed under careful experimental conditions.

Material characterization studies of growth anomalies which can occur under some B_4C whisker growth conditions has further extended the knowledge already gained in this field.

As an example, long growth runs result not in longer,high quality whiskers but rather in whiskers that are coarse and contain polycrystalline surface deposits and dendritic growths. The polycrystalline deposits exhibit an orientation which is greatly influenced by the orientation of the supporting whisker (epitaxy).

The concentric cylinder reaction chamber presently used for B_4C whisker growth will inherently produce a variety of whiskers, some with curvature and others nearly straight, some short and some long, depending upon their position in the chamber. The severity of curvature depends upon the temperature distribution within the annular region of the cylindrical chamber. Whiskers with severe curvature are weak.

V. FUTURE WORK

By mutual agreement with NASA is has been decided to emphasize and more extensively document the reinforcing potential of B_4C whiskers, (particularly those grown by using improved conditions) and defer composite fabrication to a later date. Thus an extensive study of the mechanical and chemical properties of individual whiskers will be made so that a more critical evaluation of the utility of B_4C whiskers can be reached. Also, growth studies of a more basic nature will be made to further increase whisker quality and quantity.

TABLE I. FABRICATION OF BORON CARBIDE IN ALUMINUM COMPOSITES

No.	Whisker Treatment	Die Jig Loading	Temp. °C	Pressure Lbs/in^2	Time (Min.)	Tensile Strength, psi	Remarks
BCC 6230165	-------	"V" Groove Sandwich	700°C	2000	15	4,280	Broke at grip
BCC 623265	-------	"V" Groove Sandwich	700°C	2,000	20	7,600	------------
BCC 6230365	Mixed Al powder	"V" Groove Sandwich	700°C	2,000	15	3,666	Broke at grip
BCC 6240165	Mixed Al powder	"V" Groove Sandwich	700°C	2,000	20	20,500	
BCC 6240265	Al Flake Suspension	"V" Groove Sandwich	700°C	2,000	2	14,750	
BCC 6250165	Ti-Ni Coated	Sandwich	700°C	2,000	20	16,000	
BCC 6250265	Al Flake Suspension Baked Out Acetone 220°C 2 Hours	Sandwich	700°C	2,000	20	14,300	
BCC 6280165	"	"	"	"	15	16,000	
BCC 6280165	-------	Steel Jig Sandwich	300°C	24,000	5	2,600	Broke at grip
BCC 6290165	-------	"	480°C	40,000	10	8,900	

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ACKNOWLEDGEMENTS

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